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DETERMINATION OF TOTAL IRON --COULOMETRIC METHOD: SUMMARY OF PRELIMINARY RESULTS

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ABSTRACT

The results of test measurements of a coulometric method for the determination of total iron in iron ores are described. The method is an adaptation of a draft international standard method undergoing testing by the International Standards Organization (ISO) technical committee on iron ores, Working Group 29A.

Maximum current limitations of the coulometer are exceeded with samples of the size specified in the ISO procedure. The procedure was therefore adapted to limit the currents to 500 mA by initially controlling the reduction or oxidation potential.

A second modification to the ISO procedure involved the chemical treatment prior to electrolysis. It was observed that components of some of the ores tested cause unacceptably slow electrolysis rates, presumably by poisoning the platinum electrode. In these cases it was discovered that pretreatment of the solutions with hydrofluoric acid restores these rates to acceptable values.

Tests on National Bureau of Standards (NBS) and Canadian Certified Reference Materials Project (CCRMP) reference iron ores NBS 27e, CCRMP MW-1 and CCRMP SCH-1 gave mean values of 66.63, 65.92 and 60.69 percent iron respectively, in good agreement with the certified values of 66.58, 66.08, and 60.73 percent. The overall relative standard deviation of measurements was about 0.15 percent, which is comparable to the average precision reported for volumetric iron determinations in the certification programs for SCH-1 and MW-1.

Since the precision and accuracy specifications for the coulometer in the ISO draft standard are not met with the present instrumentation and since the method has been modified significantly to accommodate the maximum current capacity of the coulometer, the value of participation in an up-coming ISO test round is queried.

KEYWORDS: Iron determination, Iron ores, Coulometry, Reference Materials, Electrochemistry

DOSAGE DU FER TOTAL - MÉTHODE COLORIMÉTRIQUE : COMPTE RENDU DES RÉSULTATS PRÉLIMINAIRES

par

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RÉSUMÉ

Le rapport fait état des résultats découlant de la vérification des mesures obtenues au moyen d'une méthode calorimétrique utilisée pour doser le fer total dans les minerais de fer. La méthode a été adaptée d'après une méthode qui doit être normalisée à l'échelle internationale. Cette dernière est présentement soumise à des essais par le Groupe de travail 29A, du Comité technique de recherche sur les minerais de fer, de l'Organisation internationale de normalisation (ISO).

Quand on a utilisé des échantillons dont la dimension était conforme à celle spécifiée par la directive de l'ISO, les limites de tolérance du courant électrique du colorimètre ont été dépassées. La méthode a donc été modifiée de façon à limiter les courants à 500 mA en contrôlant, au départ, le potentiel de réduction et d'oxydation.

La deuxième modification apportée à la méthode de l'ISO, porte sur le traitement chimique précédant l'électrolyse. On a constaté que les constituants de certains minerais qui avaient été soumis à un contrôle, ralentissaient le taux d'électrolyse de façon inacceptable et étaient probablement à l'origine de l'empoisonnement de l'électrode de platine. On a découvert que dans ces cas, le traitement préliminaire des solutions avec de l'acide hydrofluorique rétablissait les taux d'électrolyse à un niveau acceptable.

Un contrôle des minerais de fer de référence CCN 27e, PCCMR MW-1 et PCCMR SCH-1 du Conseil canadien des normes (CCN) et du Programme canadien de certification des matériaux de référence (PCCMR), a permis d'assigner à ces minerais, des valeurs moyennes de 66,63, 65,92 et 60,69 pour cent en fer, respectivement. Ces valeurs sont conformes aux valeurs certifiées qui suivent, 66,58, 66,08 et 60,73 pour cent. En général, l'écart type relatif entre les mesures a été d'environ 0,15 pour cent. Ce taux est comparable au taux moyen de précision obtenu lors du dosage volumétrique du fer dans le cadre des programmes d'homologation de SCH-1 et MW-1.

Comme l'appareillage qui existe à l'heure actuelle ne répond pas aux spécifications de la norme de précision et d'exactitude des calorimètres que l'ISO cherche à établir et, la méthode ayant été considérablement modifiée en fonction de la capacité maximale du calorimètre, l'utilité de participer au prochain essai de l'ISO est mise en doute.

TS-cle : Détermination du fer, Minerais de fer, Colorimètre, Matériaux de référence, Électrochimie.

INTRODUCTION

In 1986 the authors undertook to contribute to the ISO TC102 working group study to develop a proposed method for the coulometric determination of iron in ores. In late 1986 and early 1987 experiments were carried out to adapt the procedure to permit usage of the available equipment and carry out preliminary measurements of iron in certified reference ores to establish the performance of the modified method.

In October 1987, the fourth working draft of the coulometric procedure under development was received at CANMET along with three ore samples for participation in a test measurement round. This draft, identified as N2, is attached as Appendix I. The fourth draft contains some specifications which we are able to approach, but not strictly meet with our equipment.

The question arises: would participation in the test round represent a positive contribution to the program in view of the procedural modifications and deviations from specifications of the draft method?

The procedural adaptations and preliminary results obtained with test reference ores are discussed herein with respect to the draft standard and our ability to contribute to the measurement round.

EXPERIMENTAL: COULOMETRIC PROCEDURE AS MODIFIED FOR CANMET APPLICATION

1. EQUIPMENT

PAR model 173 potentiostat/ galvanostat

PAR Model 178 electrometer probe

PAR Model 179 digital coulometer

Cell: Standard 100 mL beaker with machined nylon top with o-ring seal; drilled to accommodate:

- auxilliary electrode compartment: 12 mm o.d. No. 4 porosity scintered glass filter tube

- Pt working electrode contact

- Reference electrode (12mm o.d.)

- Nitrogen purge tube and gas outlet

Working Electrode: Pt gauze cylinder 35 mm diameter x 20 mm

Auxilliary Electrode: two Pt gauze strip electrodes, 4 mm x 55 mm

Reference Electrode: Fisher 13-639-52 SCE.

Stirring by 25 mm x 5 mm teflon-coated magnetic stirring bar with a variac regulated stirring motor.

Gas purge: UHP grade nitrogen ; scrubbed with a vanadous chloride scrubbing train.

Calibration equipment:

Standard resistor: General Radio Type 500-B; 10 ohm = 0.05%; max. 310 mA. Calibrated at NRC ; 10.02442 ohms at 23° C. and 100 mA with 20 minute warmup.

Weston cell: Muirhead No. 242392; 1.01859 V. @ 20° C.

Digital Voltmeter: Keithley Model 177 input impedance 10 M ohm.

Stopwatch: Fisher quartz digital.

Reagents: Sodium carbonate: Anachemia anhydrous reagent, ACS lot 181221 ; Fe = 5 ug/g.

Boric Acid: Anachemia crystal reagent, ACS, lot 481116; Fe = 0.001%.

Sulphuric Acid: Allied Chemical Reagent, ACS, density 1.84; Fe = 0.2 ppm.

High purity iron: BCS 149/2 99.936% Fe.

Test iron ores:

NBS SRM 27e; 66.58 % Fe

CCRMP SCH-1; 60.73 % Fe

CCRMP MW-1 ; 66.08 % Fe

2. PROCEDURE MODIFICATIONS
(cf. Doc. ISO/TC102/SC2(WG29A)N2)

The ISO document ISO/TC102/SC2(WG29A)N2 is appended. This section describes modifications to the procedure as adopted in the application at CANMET in the test study with reference to the appropriate ISO document sections.

Doc. Item	Comment
4.2	The 0.001% Fe content of the boric acid reagent available exceeds 0.0002 % specification.
5.1	In potentiostat mode, the Model 173 current output is not limited to a max. of 600 mA. The current output is determined by the electrode reaction kinetics at the assigned potential.
5.2	The Model 179 has an integration reproducibility specification of ±2 digits in the 4-digit display. At 600 coulombs, this corresponds to ±0.033 %, exceeding the ± 0.01 % specification of the document. The Model 179 has an integration accuracy specification of ±10 digits. At 600 coulombs, this corresponds to 0.17 %, greatly exceeding the 0.01 % specification. However, the accuracy, tested with the standard resistor, was found to be +0.02 % with an estimated precision of ± 0.01 %, i.e. approaching the 0.01 % specification when a small correction to the observed coulombs is applied.
5.3	The working and auxilliary electrodes deviate from the specified areas. This change is believed to be immaterial. The auxilliary compartment frit test has heretofore not been successfully carried out. It is our experience that cycle two determinations yield lower coulombs than cycle one, typically 1 coulomb at the 600 coulomb level. It is difficult to attribute this to iron diffusion into the auxilliary; the reverse flow direction during coulometry is invariably observed; sometimes necessitating an auxilliary top-up operation during electrolysis. A salt bridge for the reference electrode was not used in our application. The RE has instead been placed

directly in the working compartment.

UHP nitrogen has been used instead of argon. A vanadous scrubbing train (L. Meites, "Polarographic Techniques, Second Edition", page 89, 1964) was used in line to remove traces of oxygen.

A constant voltage line transformer was not used. The model 173 can tolerate ±10 % fluctuations in line voltage with less than 100 uV change in output.

7.4.1 A crucible lid was used. Residue was normally observed on this lid following fusion.

Normally, sample decompositions were carried out several days prior to coulometry. On the day of coulometry, the solution was reheated to the boiling point, stirred and cooled.

Two test ores (NBS 27e and MW-1) were found to give slow reductions and oxidations. It was speculated that this was due either to electrode poisoning or adsorption of iron on insoluble material observed in the solution (e.g. silica). Tests showed that pre-treatment of the solution with hydrofluoric acid restored normal reduction and oxidation periods. The following procedure was adopted for these cases: add 1 mL of 48 % HF to the solution and stir 3 minutes; heat solution to near boiling and then cool.

7.4.3 Reduction stage.
7.4.4 Oxidation stage.

The coulometer has a current limitation of 500 mA on the optimum current range. The potentiostat is not current limiting in controlled potential mode. Initial currents greatly exceed 500 mA with the quantities of iron present in 0.5 g ore samples at the 0.2 V and 0.7 V potentials specified for reduction and oxidation respectively. To perform coulometry with these levels of iron with this apparatus in controlled potential mode it is necessary to gradually adjust the reduction (oxidation) potential towards the final value during the course of electrolysis, keeping the current below 500 mA.

The modified procedure adopted is:

Reduction: -Set initial potential at 0.500 V.

-Reset coulometer.

-Turn cell on.

-Adjust potential towards 0.200 V to yield approx. 490 mA (< 500 mA).

-Periodically adjust potential towards 0.200 V keeping the current in the range 400 to 500 mA.

-When 0.200 V is achieved, allow the current to decay to 120 uA.

Oxidation: -Adjust the potential (approximately to 0.202 V) to yield zero current. Reset the coulometer.

-Adjust the potential towards 0.700 V until the current approaches, but does not exceed 500 mA.

-Periodically adjust the potential towards 0.700 V to maintain the current in the range 400 to 500 mA.

-When 0.700 V is achieved, allow the current to decay to about 500 uA. Record the coulometer reading. Precisely at the next decimal digit change, reset the coulometer.*

-Allow the current to decay to 120 uA. Record the accumulated coulombs and then turn the cell off. Add 0.1 plus the observed coulombs to the previously recorded value to obtain the total for the iron measurement to the nearest 0.01 coulombs .

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* This step is necessary to achieve reading to the nearest 0.01 coulomb.

7.5.2 Integration factor, f.

The voltage/ frequency converter is specified to drift < 0.005 % per °C; therefore temperature compensation is regarded as unnecessary.

The coulometer was calibrated using the standard resistor as a dummy cell and the Model 173 potentiostat as a stable voltage source. The voltage

output is only specified as accurate to 1 mV. It was therefore necessary to measure the actual output using a digital voltmeter (DVM) readable to 0.1 mV to enable calibration to an accuracy of 0.01 % at 1 V. The accuracy of the DVM (which has an input impedance of 10 Megohms) was confirmed by measuring the voltage of a Weston cell). It was found to be accurate to 0.1 mV at the 1 V measurement level.

For seven measurements of 1000 s each at 1000 mV and 10 ohm resistance (100 coulombs):

$$Q_{actual}/Q_{obs} = 0.9998 \pm 0.0001$$

Thus the integration correction factor is taken as

$$f = 0.9998.$$

7.5.1 Calibration Factor, F.

BCS 149/2 high purity iron was used to establish the calibration factor, F,

$$F = W_t / W_f$$

where W_t is grams iron taken and W_f is grams iron found. By subtraction of known impurities, the iron fraction of BCS 149/2 is 0.9993_6 .

Samples of 0.3 gram mass were dissolved in 25 % v/v sulphuric acid and carried through the redox procedure. Results are summarized in Table 1.

Table 1 - Measurements of pure iron samples: determination of the calibration factor, F.

Run	W_t	$Q_{obs-blank}$*	W_t / W_f**
1	0.300058	517.05	1.002834
2	0.300053	516.46	1.003958
3	0.299678	516.23	1.003140
4	0.299143	515.76	1.002290
5	0.300108	517.47	1.002197
6	0.300897	517.33	1.005102
		mean:	1.003253
		SD:	0.001109
		rsd,%:	0.11

*The sulphuric acid blank was 0.19 = 0.02 coulombs.
**W_f = Q x f x 55.847 / 96487 ; where f = 0.9998.

The calibration factor F is thus taken as

F = 1.003253

8. Calculation of results

$$Fe\ \% = (Q_{obs} - Q_{blank}) \times 55.847 \times 100 \times F \times f / (96487 \times M)$$

where: Q_{blank} is the coulombs obtained from a blank carried through the fusion procedure

M is the weight in grams of ore taken

Q_{obs}, F and f are defined above.

TEST RESULTS

Blanks carried through the fusion procedure gave the following values: (coulombs) 0.51, 0.40, 0.41, 0.66, 0.37. A blank value for correction of test results of 0.40 was taken. The results for total iron in reference ores obtained by coulometric analysis as described above are compiled in Table 2.

Table 2 - Test results for reference iron ores.

Ore	HF* treatment?	grams taken	Coulombs, net (oxid.)		Iron, found %
SRM 27e	yes	0.48520	556.62		66.603
	yes	0.49280	565.60		66.633
	yes	0.57036	654.29		66.600
	no	0.49994	574.10		66.670
	no	0.50119	577.63		66.912**
				mean:	66.627
				s.d.:	0.033
MW-1	yes	0.49861	565.38		65.832
	yes	0.50237	571.94		66.097
	yes	0.50457	572.57		65.881
	yes	0.49840	565.40		65.862
				mean:	65.918
				s.d.:	0.121
SCH-1	no	0.49824	520.55		60.656
	yes	0.50461	527.77		60.721
				mean:	60.689

* See 7.4.1, above.

** Declared outlier measurement; suspected inappropriate background subtracted due to inordinately long oxidation electrolysis.

The certified values for the reference ores are:

SRM 27e	66.58 %	± 0.044 %	(15 LABS)
MW-1	66.08 %	± 0.115 %	(15 LABS)
SCH-1	60.73 %	± 0.180 %	(23 LABS),

where the = values shown are the std. deviations of participating laboratory mean values in the certification program.

DISCUSSION

At this juncture, test measurements are not extensive. The data are presented since a decision is necessary as to the benefit of participation in the ISO test round. Results for this round are required by the end of February, 1988.

The limited test data indicate that iron can quantitatively be measured in ore materials using the modified test procedure. The mean values found for SRM27-e, MW-1 and SCH-1 are in reasonable agreement with the recommended values, lying within 1.5 standard deviations of the distributions of participating laboratory values in each case.

The data are limited with respect to estimation of a typical relative standard deviation (RSD) associated with single determinations using the modified procedure. From the pure iron measurements and the MW-1 determinations, it would appear that the RSD may be of the order 0.1 to 0.2 percent for determinations of 0.3 gram quantities of iron. This would appear to be comparable to average in-laboratory RSDs for volumetric determination procedures observed in the MW-1 and SCH-1 certification projects (0.10 % and 0.13 %, respectively).

It is noteworthy that the results for determination of pure iron samples are consistently low by 0.3 percent (leading to the correction factor, F = 1.00325). This suggests that the reduction and oxidation cycles are not totally reversible, even in the absence of possible interferants, or that non-electrode (chemical) oxidation proceeds simultaneous to the electrochemical process. In repeated cycle experiments (reduction/oxidation/reduction/ oxidation/etc.) successively lower coulomb values are observed for each oxidation, perhaps supporting the former interpretation.

The ISO document indicates that losses may be associated with diffusion of iron-containing solution into the auxilliary compartment, and that with a suitable frit coulombs upon recycling should reproduce within 0.02 %. Typically we observed 0.1 to 0.2 percent losses in iron value with a re-cycle. There is generally an observable positive flow from the auxilliary compartment to the working compartment during the experiments conducted to date, usually requiring topping-up of the auxilliary solution following a cycle.

To employ the Model 173 / Model 179 coulometry system with this procedure it has been necessary to manually control the maximum current during the course of the experiment. This has been done by stepping the potential towards the final value during the experiment. In effect, the first part of the electrolysis is controlled current

coulometry while the finish is controlled potential coulometry.

The draft ISO procedure employs a potentiostat capable of limiting the current. The mechanism of this electronic control is unknown to the authors. If current limitation is achieved by modifying the applied potential, the manual control applied herein is analogous. If the potential is truly maintained at the final fixed value, then the procedure is somewhat different.

The procedure with manual current control is impractical for general application since it requires constant operator attention over the span of the electrochemical titration, which is normally about one hour per sample.

Current decay profiles observed for two samples of MW-1 are shown in Figure 1. These profiles are for the oxidation half of the cycle; the reduction half is similar. MW-1 is one ore where slow electrode kinetics were consistently observed. The oxidation half-cycle in this case took about 75 minutes to reach the 120 µA background level. The prior reduction half-cycle took 68 minutes to reach this level.

It was initially suspected that the slow electrolysis properties may be due to an adsorption of iron on insoluble material in the solution which was inferred to be silica. It was speculated that slow release of the adsorbed iron contolled the electrolysis rate. Treatment with hydrofluoric acid was therefore carried out to dissolve residual silica, and this restored normal electrolysis rates, e.g. Figure 1B.

Subsequent tests with silica added to pure iron failed to show slow electrolysis properties. It is now suspected that some other component of MW-1 is poisoning the platinum electrode. This component remains unidentified, but its effect is evidently removed by a preliminary treatment with hydrofluoric acid as described under 7.4.1, above.

CONCLUSION

Participation in the ISO measurement round is evidently contra-indicated for the following reasons:

1. The available coulometer does not meet the specifications for precision or accuracy of the ISO draft procedure item 5.2.

1a. The coulometer precision obtainable is estimated as 0.03% at 600 coulombs and the accuracy attainable (by calibration with a standard resistor and accurate voltage source) is estimated as 0.03% .

2. The potentiostat is not current-limiting (as required in item 5.1) and the iron quantities cause currents which exceed the capabilities of the coulometer at the specified potentials during the initial part of the oxidation or reduction.

2a. Currents can be limited to the coulometer capability by adjustment of the potential during the initial part of the electrolyses. This procedure is impractical for general application since constant operator attention is required.

If the deviations from the standard procedure and its specifications as summarized in 1a. and 2a. above are regarded as acceptable to ISO, then it may be worthwhile to measure and report the test samples.

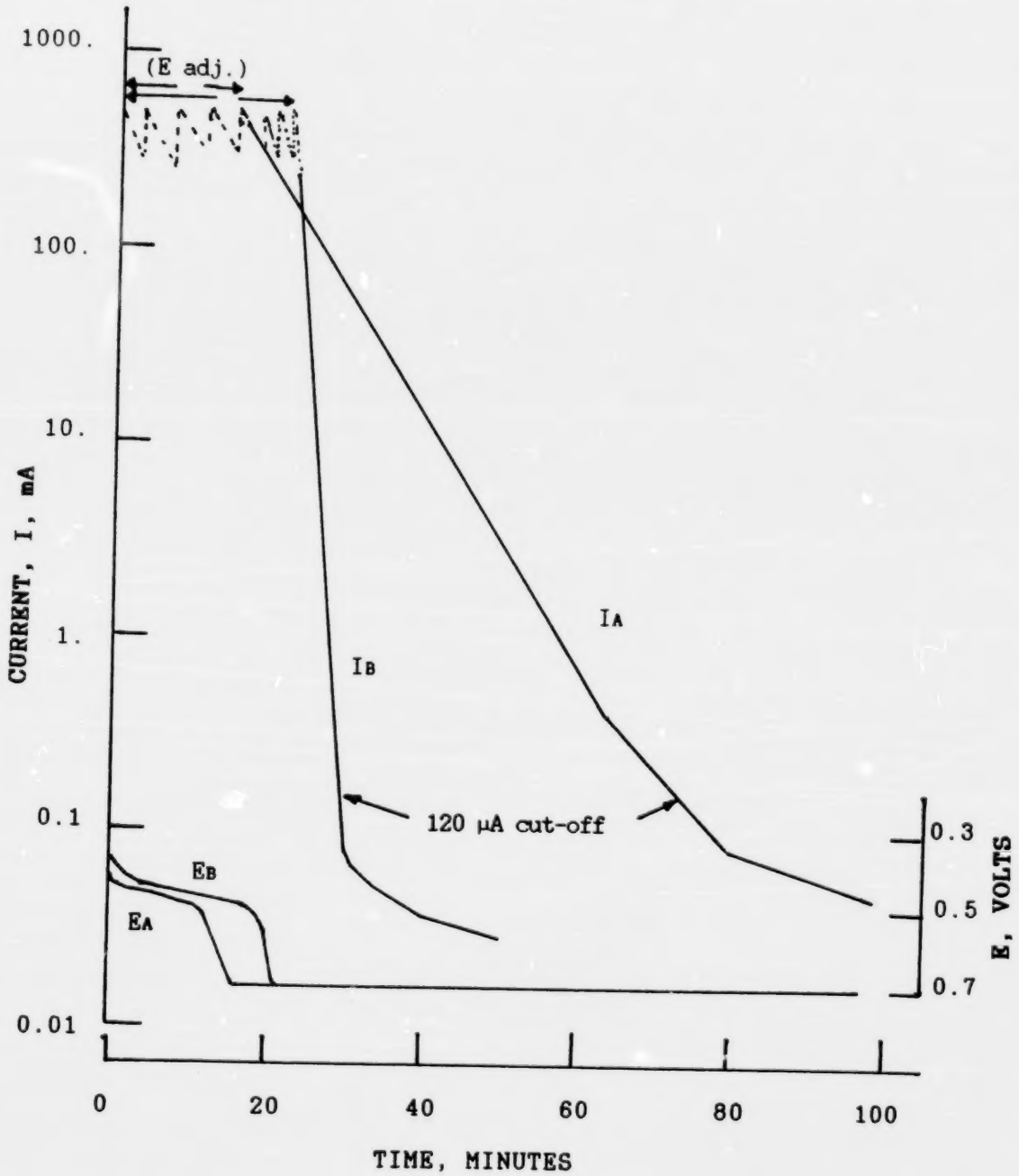

Figure 1 - Comparison of current decay behaviour during Fe(II)/Fe(III) oxidation coulometry of 0.5 gram samples of MW-1 iron ore. A. Sample decomposed and dissolved as per ISO procedure. B. Dissolved sample treated with 1 mL 48 % HF prior to coulometry.

APPENDIX

ISO DRAFT INTERNATIONAL STANDARD FOR THE COULOMETRIC DETERMINATION OF TOTAL IRON IN IRON ORES

(ISO DOCUMENT ISO/TC102/SC2(WG29A) N2)

DRAFT INTERNATIONAL STANDARD

Iron ores - Determination of Total Iron Content - Coulometric Method

(FOURTH WORKING DRAFT)

1. Scope

This draft International Standard specifies a method for the determination of total iron content in iron ores using controlled potential coulometry.

The method is applicable to a concentration range of 30 to 72 % (m/m) of iron in natural iron ores and iron ore concentrates and agglomerates, including sinter products.

2. Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of ISO maintain registers of currently valid International Standards.

ISO 3081-1986 Iron ores - Increment sampling - manual method

ISO 3082-1987 Iron ores - Increment sampling - mechanical method

ISO 3083-1986 Iron ores - Preparation of samples

ISO 7764-1985 Iron ores - Preparation of predried test samples for chemical analysis

3. Principle

Fusion of the sample with sodium carbonate-boric acid mixture and extraction of the melt with sulphuric acid. Reduction with the working electrode at a potential of 0.2 V versus a saturated calomel electrode followed by oxidation of the Fe (II) to Fe (III) at a potential of 0.7 V versus a saturated calomel electrode. The amount of electrical charge passed during the oxidation stage is measured with an electronic integrator and is used to calculate the total iron content.

4. Reagents

During the analysis, use only reagents of recognised analytical grade, and only distilled water or water or equivalent purity.

4.1 Sodium carbonate, anhydrous, high purity (minimum assay 99.9 %), with iron content of less than 0.0005 %.

4.2 Boric acid, high purity (minimum assay 99.8 %), with iron content of less than 0.0002 %.

4.3 Sulphuric acid, p 1.84 g/ml

4.4 Sulphuric acid, 25 % V/V

To 600 ml of water cautiously add 250 ml sulphuric acid (p 1.84 g/ml) whilst stirring. Cool, dilute to 1 litre with water and mix.

4.5 Sulphuric acid, 16 % V/V

To 80 ml of water cautiously add 16 ml sulphuric acid (p 1.84 g/ml) whilst stirring. Cool, dilute to 100 ml with water and mix.

4.6 Nitric acid, p 1.42 g/ml

4.7 Hydrogen peroxide, 6 % m/V

5. Apparatus

Ordinary laboratory apparatus, and

5.1 Potentiostat - Standard laboratory potentiostat with current output limited to a maximum of 600 mA.

5.2 Integrator - Any instrument capable of integrating 600 coulombs to the nearest 0.01 C with an overall accuracy better than 0.01 %. The voltage drop across a standard 2 Ω resistor converts a voltage integrating instrument into a current integrator.

5.3 Coulometric cell - A 150 ml tall-form beaker closed with a rubber bung containing the following components, as shown in figure 1.

a) Working electrode - Cylindrical platinum gauze 40 mm diameter by 40 mm high attached to a platinum wire stem.

Condition the electrode before use by boiling in nitric acid (4.6) for about 15 s.
Carry out this operation at the back of a fume cupboard and use eye protection.

b) Auxiliary electrode compartment - This consists of a glass tube 20 mm diameter, sealed at the lower end with a No. 4 porosity sintered-glass disc. The sinter shall be capable of carrying a current of 600 mA without causing the solution to boil at its surface.

Test the suitability of the sintered glass disc by carrying out a determination in accordance with 7.4. Then, without removing the solution, repeat the reduction and oxidation stages, 7.4.3 and 7.4.4 respectively. If there has been no diffusion of iron into the auxiliary electrode compartment the total coulombs recorded should remain the same. A difference between the two readings of less than 0.1 C in 500 C indicates that the sintered-glass disc is satisfactory.

Inside the tube a 6 mm wide platinum strip forms the auxiliary electrode. This is folded double, about 15 mm from the end, in order to increase the surface area. A fine acid resistant plastic tube is inserted into the glass tube for the purpose of bubbling argon through the elecrolyte. To avoid diffusion of iron into the auxiliary electrode compartment the electrolyte level at the start of the determination should be 30 mm above the level of the main solution.

c) Reference electrode - A saturated calomel electrode, refilled with saturated KCL and solid KCL before each determination. Contact between the reference electrode and the electrolyte is made via a salt bridge. NOTE - A remote type saturated KCl electrode is available commercially.

d) Argon inlet tube - A glass inlet tube to allow a stream of high purity argon (< 5 ppm oxygen) to flow over the surface of the electrolyte without bubbling through it. The argon escapes at the working electrode entry port.

e) Stirrer Bar - PTFE coated 'STAR' type stirring bar.

5.4 Magnetic stirrer

5.5 Standard 2Ω resistor - Tolerance within 0.01 % of nominal value.

5.6 Weston Standard Voltage Cell - With attached thermometer to permit temperature correction. 1.0186 V at 20 °C (± 0.00004 V per °C).

5.7 Constant Voltage Transformer - 250 W.

5.8 Argon cylinder - High purity argon (5 ppm oxygen).

5.9 Pure Platinum crucibles - 40 mm diameter, 15 ml capacity.

5.10 Muffle furnace - Capable of operating at 1000 ± 20 °C.

NOTES

1. The apparatus is arranged as shown in figure 2. The potentiostat and integrator should be connected to the mains supply via a constant voltage transformer.

2. Set up the potentiostat and the integrator according to the manufacturer's instructions. Allow sufficient time to warm up (approx. 30 min). Set up the applied potential on the potentiostat to 0.200 V for the reduction stage. If a second channel is available on the potentiostat set this to an applied potential of 0.700 V in readiness for the oxidation stage. Initially the cell switch should be in the 'OFF' or 'DUMMY CELL' position.

3. The procedure may be automated by use of a microprocessor to control the operation of the equipment.

6. Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 um particle size which has been taken in accordance with ISO 3081 or ISO 3082 and prepared in accordance with ISO 3082 or ISO 3083. In the case of ores with significant contents of combined water or oxidizable compounds, use a particle size of minus 160 µm.

NOTE - A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

6.2 Preparation of predried test samples

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a manner that it is representative of the whole contents of the container. Dry the test sample at 105 ± 2 °C as specified in ISO 7764. (This is the predried test sample.)

7. Procedure

7.1 Number of determinations

Carry out the analysis at least in duplicate, independently, on one predried test sample.

NOTE - The expression 'independently' means that the second and any subsequent result is not affected by the previous result(s). For this particular analytical method, this condition implies that the repetition of the procedure shall be carried out either by the same operator at a different time or by a different operator including, in either case, appropriate recalibration.

7.2 Blank test and check test

In each run, one blank test and one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analysis of the ore sample(s) under the same conditions. A predried test sample of the certified reference material shall be prepared as specified in 6.2 (see the note).

When the analysis is carried out on several samples at the same time, the blank value may be represented by one test, provided that the procedure is the same and the reagents are from the same reagent bottles.

When the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified material may be used.

NOTE - The certified reference material should be of the same type as the sample to be analysed and the properties of the two materials should be sufficiently similar to ensure that in either case no significant changes in the analytical procedure would become necessary.

7.3 Test portion

Taking several increments, weigh, to the nearest 0.00001 g, approximately 0.5 g of the predried test sample obtained in accordance with 6.2, using a non-magnetic spatula.

NOTE - The test portion should be taken and weighed quickly in order to avoid reabsorption of moisture.

7.4 Determination

7.4.1 Decomposition of test portion

Weigh 1.8 g sodium carbonate (4.1) and 1.2 g boric acid (4.2) into a platinum crucible and mix. (See Notes 1 and 2). Fuse the mixture over a flame and cool. Place the test portion into the platinum crucible containing the flux, fuse over a flame to dissolve as much of the sample as possible and transfer the crucible into a muffle furnace heated at 1000 $\pm$ 20 °C. After 20 minutes remove the crucible and cool.

NOTES
1. A crucible lid may be used during the fusion procedure.
2. At all times ensure that the crucible is placed on a clean dry surface.

Transfer the crucible and contents to a 150 ml tall-form beaker and add 40 ml sulphuric acid (4.4). Heat gently until all the solid melt has dissolved. Remove the crucible, wash, collecting all the washings in the main solution (see Note 3). Allow to cool.

NOTE 3
If undissolved matter is visible reject the sample and repeat. Ores containing high levels of silicon and calcium can be analysed in the presence of insoluble silica or calcium sulphate. An ultrasonic bath can be used to aid the dissolution of high calcium ores.

7.4.2 Preparation of coulometric cell

NOTE - Take extreme care to avoid contamination at all stages. The laboratory temperature should not vary by more than 1°C during the determination.

Immerse the platinum working electrode and the stirring bar in the solution in the beaker. Add 10 ml sulphuric acid (4.5) to the auxiliary electrode compartment and place the rubber bung carrying the auxiliary electrode compartment, calomel electrode etc. in position on the beaker.

Place the beaker on the magnetic stirrer and connect the working, auxiliary and reference electrodes to the potentiostat-integrator system (see figure 2). Connect the argon supply to the gas inlet tube and adjust the flow-rate to about 250 ml/min.

Arrange a by-pass, to allow argon to flow at a rate of about 100 ml/min into the auxiliary electrode compartment, by means of a T-piece and screw clip on the cell inlet side. Switch on stirrer and adjust to its maximum stable speed.

7.4.3 Reduction stage

Set the potentiostat to + 0.200 V and the current range to 2000 mA. Switch in the cell and commence reduction of iron to the Fe (11) state. As reduction proceeds adjust the current range switch. The end of the reduction stage is indicated when the current has decayed to 120 µA. Return the cell current range switch to the 2000 mA range.

7.4.4 Oxidation stage

Press the 'Re-set' button on the integrator to clear any previous reading and change the set potential of the potentiostat to + 0. 700 V. An initial oxidising current of 500 mA is produced which eventually decays to a residual current of 120 µA when all of the iron is in the Fe (111) stage. As the oxidation proceeds the current range switch should be adjusted to accommodate the lower currents.

Note the integrator reading to the nearest 0.01 coulomb and switch the potentiostat to 'Dummy Cell'.

Disconnect the cell and prepare the electrodes for the next determination. Carry out a 'Blank' determination.

7.5 Calibration

7.5.1 Calibration Factor, F

Determine a calibration factor F, as follows.

Find the 'True' Fe value of pure iron wire by determining the values for oxygen, nitrogen, carbon, sulphur and for the total metals other than iron, and subtracting the sum of these impurities from 100 %.

Determine the 'Apparent' Fe content of the pure iron wire by weighing, to the nearest 0.00001 g, approximately 0.3 g of the pure iron wire and dissolving in 40 ml sulphuric acid (4.4). Cool and add 1 ml of hydrogen peroxide (4.7) to oxidise the majority of the iron. After 10 minutes, boil to destroy any remaining hydrogen peroxide. Dissolve 3 g of fused sodium carbonate - boric acid mixture in the solution. Transfer to the coulometric cell and analyse in the same way as for the iron ore sample.

The 'Apparent' Fe content is calculated from the expression

$$\frac{Q \times 55.847 \times 100}{96487 \times M}$$

(See 8.1 for definitions of Q and M.)

The Calibration factor F is then given by $\frac{\text{'True' Fe content}}{\text{'Apparent' Fe content}}$

7.5.2 Integration Factor, f

In modern commercial integrators a standard 2 Ω resistor can be incorporated within the unit, and this can be switched into the circuitry to convert voltage to current. A standard voltage generator unit can also be incorporated to give a continuous automatic correction of voltage to a standard level, which will obviate the need for manual correction for temperature compensation.

However, if the integrator is not capable of automatic temperature compensation this shall be carried out manually (in the voltmeter mode) using a Standard Weston Cell. Temperature correction is 1.0186 V at 20 °C. ($\pm$ 0.00004 V per °C). Under these circumstances an additional calibration factor shall be used in the final calculation, i.e. f_1, the Integration Factor. f_1 can be calculated by connecting a Standard Weston Cell to the integrator and noting the reading obtained. At the same time the true value for the cell, at the temperature used, can be calculated.

$$f_1 = \frac{\text{True cell voltage}}{\text{Mean of True and observed voltages}}$$

If the integrator is capable of automatic temperature compensation, then for all practical purposes $f_1 = 1$.

8. Expression of results

8.1 Calculation of total iron content

The total iron content, as a percentage by mass, is calculated from the following equation :

$$\text{Fe } \% \text{ (m/m)} = \frac{Q \times 55.847 \times 100}{96487 \times M} \times F \times f_1$$

where

Q is the integrator reading in coulombs, corrected for the 'BLANK';
M is the mass in grams of the test portion;
F is the Calibration Factor (7.5.1).
f_1 is the Integration Factor, used only if manual temperature correction is carried out. (See 7.5.2).

8.2 General treatment of results

To be added later.

9. Test report

The test report shall include the following information :

a) reference to this International Standard;

b) details necessary for the identification of the sample;

c) result of the analysis;

d) reference number of the result;

e) any characteristics noticed during the determination and any operations not specified in this International Standard which may have had an influence on the results, either for the test sample or the certified reference material(s).

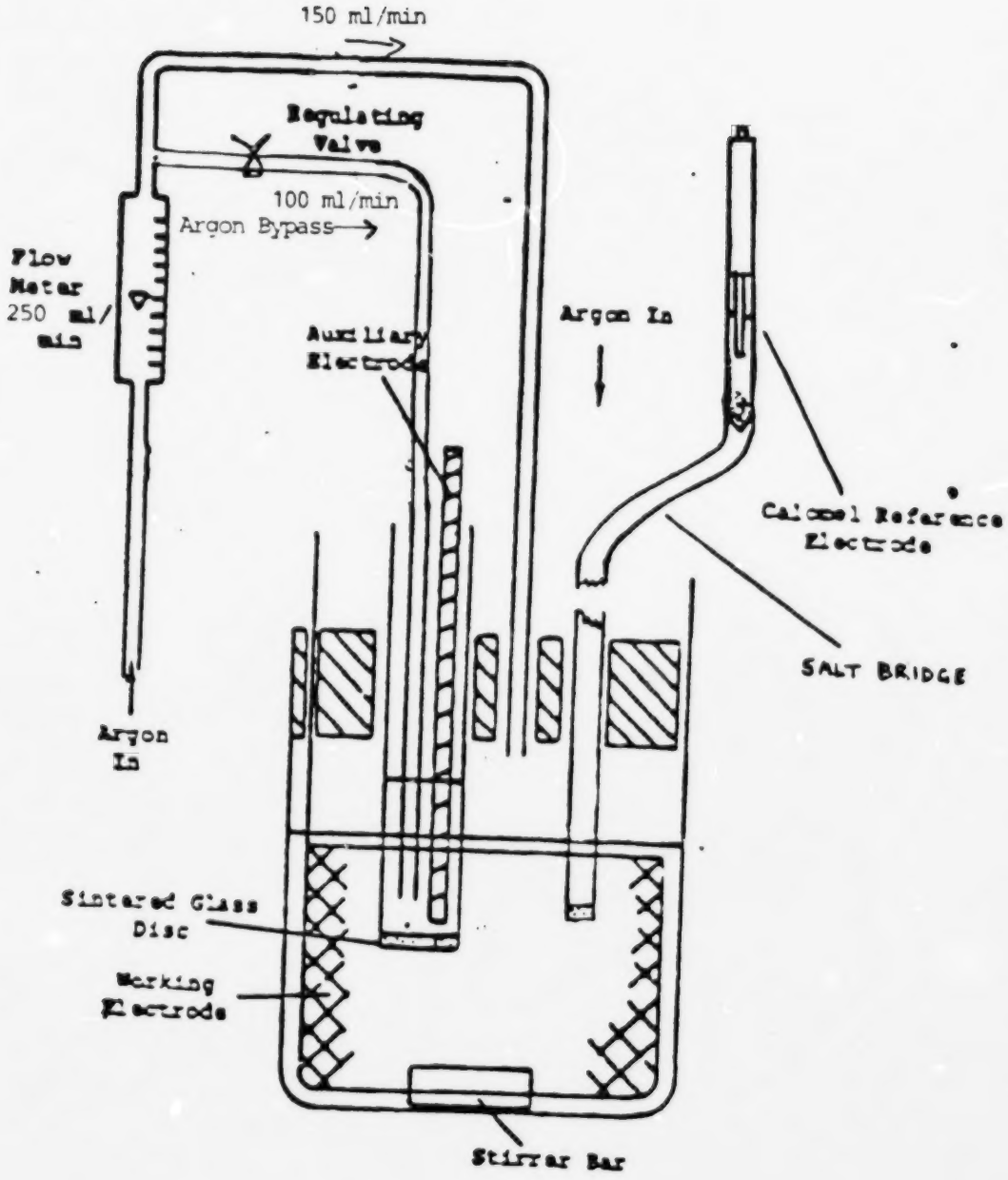

Figure 1. Coulometric cell

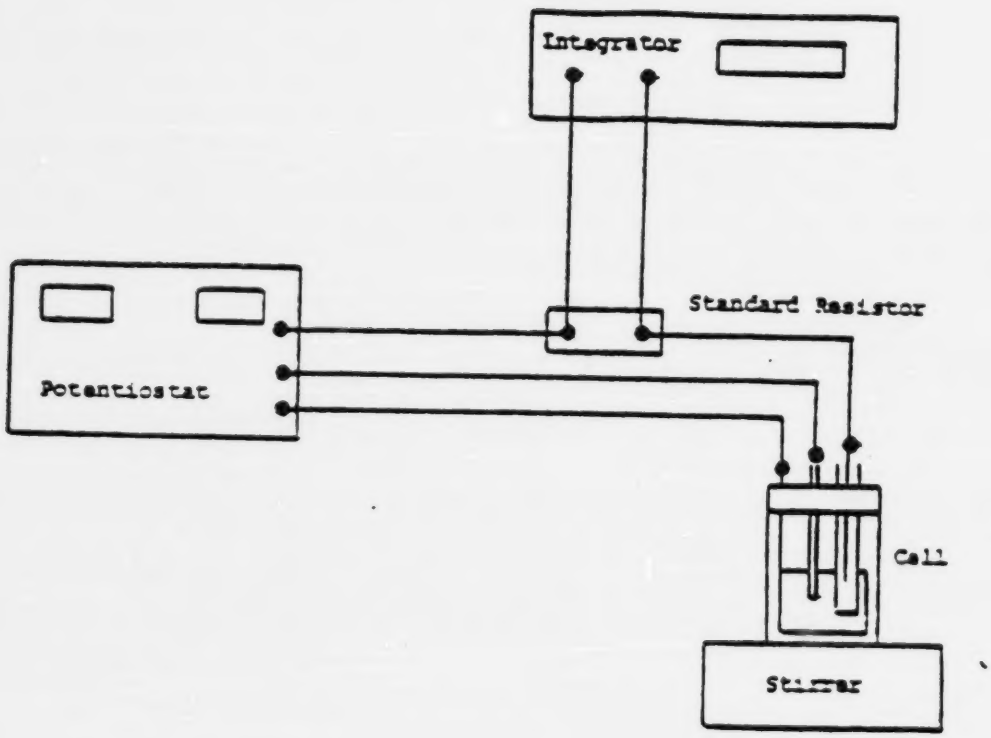

Figure 2. Coulometric apparatus